



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁵ : C07C 395/00, 391/00	A1	(11) International Publication Number: WO 90/15796 (43) International Publication Date: 27 December 1990 (27.12.90)
(21) International Application Number: PCT/GB90/00894 (22) International Filing Date: 8 June 1990 (08.06.90) (30) Priority data: 8913799.6 15 June 1989 (15.06.89) GB (71) Applicant (for all designated States except US): THE SECRETARY OF STATE FOR DEFENCE IN HER BRITANNIC MAJESTY'S GOVERNMENT OF THE UNITED KINGDOM OF GREAT BRITAIN AND NORTHERN IRELAND [GB/GB]; Whitehall, London SW1A 2HB (GB). (72) Inventors; and (75) Inventors/Applicants (for US only) : COLE-HAMILTON, David [GB/GB]; Chemistry Department, The Purdie Building, St Andrews, Fife KY16 9ST (GB). McQUEEN, Alisdair, Ewan, David [GB/GB]; 37 Fife Park, St Andrews KY16 9UE (GB). MULLIN, John, Brian [GB/GB]; The Hoo, Brockhill Road, West Malvern, Worcestershire WR14 4DL (GB).		(74) Agents: BECKHAM, Robert, William et al.; Ministry of Defence, Patents 1A, Room 2014, Empress State Building, Lillie Road, London SW6 1TR (GB). (81) Designated States: AT (European patent), BE (European patent), CH (European patent), DE (European patent)*, DK (European patent), ES (European patent), FR (European patent), GB, GB (European patent), IT (European patent), JP, LU (European patent), NL (European patent), SE (European patent), US. Published <i>With international search report.</i>
(54) Title: METHOD FOR PREPARATION OF ORGANO-TELLURIUM AND SELENIUM COMPOUNDS		
(57) Abstract Methods for the preparation of a tellurium or selenium compound of formula Ra M Rb wherein M is tellurium or selenium and Ra and Rb are different C ₁₋₂₀ alkyl, alkenyl or aryl groups are provided in which a compound of formula (Ra) ₂ M ₂ is reacted with a compound of formula (Rb) ₂ M in each compound M being the same. Compounds of formula RaMMRb may also be isolated as an intermediate. Ra M Rb compounds are useful as precursors for metal organic vapour phase epitaxy processes.		

DESIGNATIONS OF "DE"

Until further notice, any designation of "DE" in any international application whose international filing date is prior to October 3, 1990, shall have effect in the territory of the Federal Republic of Germany with the exception of the territory of the former German Democratic Republic.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	ES	Spain	MC	Monaco
AU	Australia	FI	Finland	MG	Madagascar
BB	Barbados	FR	France	ML	Mali
BE	Belgium	GA	Gabon	MR	Mauritania
BF	Burkina Faso	GB	United Kingdom	MW	Malawi
BG	Bulgaria	GR	Greece	NL	Netherlands
BJ	Benin	HU	Hungary	NO	Norway
BR	Brazil	IT	Italy	R	Romania
CA	Canada	JP	Japan	SD	Sudan
CF	Central African Republic	KP	Democratic People's Republic of Korea	SE	Sweden
CG	Congo	KR	Republic of Korea	SN	Senegal
CH	Switzerland	LI	Liechtenstein	SU	Soviet Union
CM	Cameroon	LK	Sri Lanka	TD	Chad
DE	Germany, Federal Republic of	LU	Luxembourg	TG	Togo
DK	Denmark			US	United States of America

METHOD FOR PREPARATION OF ORGANO-TELLURIUM
AND SELENIUM COMPOUNDS

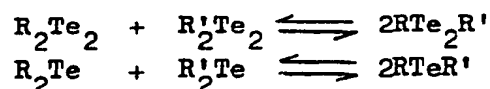
This invention relates to a method for the preparation of organo-tellurium and selenium compounds in which the tellurium or selenium is combined with two different organic groups. In particular the invention relates to a method for preparation of
5 dialkyls and diaryls in which the tellurium or selenium is combined with two different alkyl or aryl groups, termed herein unsymmetrical dialkyls or diaryls.

The Group 16 metals Tellurium and Selenium are important in semi-conductor technology for example in the preparation of the
10 infra red detector material cadmium mercury telluride (CMT) and for use in light sensing switches respectively. Frequently these metals or in particular their compounds such as CMT are deposited on substrates by the process of Metal-Organic Vapour Phase Epitaxy (MOVPE) which involves vapour phase decomposition of a volatile organic
15 compound of the metal, most usually a dialkyl. Dialkyls have the advantages that as well as being volatile they can be easily purified by formation of adducts which can be easily decomposed to form the pure dialkyl. For example GB-A-850955 describes purification by formation of adducts with Group 15 compounds, and
20 PCT/GB88/01062 describes purification by formation of adducts with Group 11 or 12 metal compounds.

Unsymmetrical dialkyls of tellurium and selenium are believed to be advantageous for MOVPE because they have the potential for combining high volatility with low temperatures for deposition
25 of the desired material. These properties have tended to be incompatible in dialkyls where the two alkyl groups are the same (ie "symmetrical dialkyls").

Although many methods of preparation of symmetrical dialkyls of tellurium and selenium are known (eg US 1578731; Synthetic
30 Communications 12(3), 163-165, (1982); J Organometallic Chemistry 255, 61-70, (1983); GB-A-850955; SU-A-371216; PCT/GB88/01065 (not yet published)) little has been done to develop convenient methods of preparation of the unsymmetrical dialkyls.

Exchange reactions of the type:



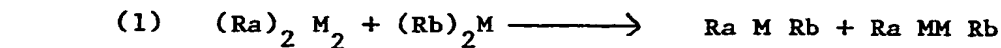
are known, but neither of these is a useful synthetic pathway as the most volatile component of the mixture is a symmetrical compound which will distil preferentially on attempting to separate the components by fractional distillation.

5 Organometallics 2, 305-307, (1983) describes a method for preparation of unsymmetrical dialkyl tellurides and phenyl-alkyl tellurides and selenides by the reaction of ditellurides or diphenyl diselenide with a Grignard Reagent or an alkali metal alkyl in an ether solvent. A titration-type procedure is used, and clearly this introduces inconvenience. Furthermore Grignard Reagents and alkali metal alkyls are known to be quite sensitive to atmospheric hydrolysis, with the consequent risk of contamination. Grignard Reagents, such as ethyl magnesium bromide also introduce the possibility of contamination of the product by halogens, which can be very deleterious in semiconductor materials.

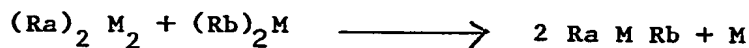
There is therefore a need for an improved method for preparation of unsymmetrical dialkyls and/or diaryls.

The method of this invention provides a method for the preparation of a tellurium or selenium compound of formula Ra M Rb wherein M is tellurium or selenium and Ra and Rb are different C₁-20 alkyl, alkenyl or aryl groups, in which a compound of formula (Ra)₂ M₂ is reacted with a compound of formula (Rb)₂ M, in each compound M being the same, followed by isolation of the product Ra M Rb.

25 It is believed that (in the case of tellurium dialkyls at least) an intermediate ditelluride or diselenide Ra MM Rb is initially formed together with Ra M Rb, and this intermediate then decomposes on heating to form Ra M Rb and the metal M, ie:



The overall reaction therefore being:



35 It is therefore preferred to carry out the method of the invention in two stages, firstly to allow the (Ra)₂ M₂ and (Rb)₂ M to react at a lower temperature, especially at around room temperature (15-30°C), and then in a second stage to heat

the reaction mixture to a higher temperature at which the intermediate decomposes.

In an unsymmetrical product Ra M Rb, clearly one of Ra or Rb may have a higher molecular weight than the other. It is known
5 that generally the higher the molecular weight of the alkyl, alkenyl or aryl group in a tellurium or selenium alkyl, alkenyl or aryl, the lower is the volatility of the compound, and furthermore that ditellurides or diselenides are generally less volatile than the corresponding compound containing one tellurium or selenium atom.

10 Therefore in the method of the invention it is preferred that if possible the combinations of starting materials $(Ra)_2M_2$ and $(Rb)_2M$ are chosen that the boiling point of the product Ra M Rb is lower than that of both starting material, so that the equilibrium of the reaction is encouraged toward Ra M Rb formation. It is also
15 preferred that if Ra and Rb have different molecular weights, then Ra should have the lower, so that the effect of the lighter Ra in increasing volatility is to some extent compensated by its being present in the ditelluride or diselenide.

Preferably approximately stoichiometric quantities of the two
20 reactants are used. It is also preferred that the first, lower temperature stage is performed in the dark. No solvent or diluent appears to be necessary for either step of the reaction, but in some cases (eg to encourage mixing of the reactants) conventional solvents such as ethers or alkanes may be used. It is preferred to
25 carry out both stages of the reaction under an inert atmosphere such as nitrogen or in vacuo.

Advantageously after the first stage, solvents, volatile impurities and/or side products (if present) may be removed under reduced pressure, and then heat applied in the second, higher
30 temperature, stage both to decompose the intermediate and to distil off the Ra M Rb product from the metal M.

The Ra M Rb product may then be further purified by conventional methods such as fractional distillation or via adduct formation as mentioned above. For example when Ra and Rb are both
35 alkyl, traces of the symmetrical dialkyls may be formed, which can be easily removed by fractional distillation.

The method of the invention may of course be used as an improved method of preparation of an unsymmetrical ditelluride or diselenide of formula Ra MM Rb. To do this the above method of the invention is performed at a temperature at which decomposition of RaMMRb does not occur or occurs slowly enough for the RaMMRb product to be isolated, for example at about room temperature, followed by isolation of the product RaMMRb. The RaMMRb product may for example be isolated by removal of any RaMRb by fractional distillation. Although RaMMRb is likely to suffer from the disadvantage of being less volatile than RaMRb it may nevertheless find uses such as in MOVPE in certain applications.

The method of the invention is applicable to the preparation of compounds in which Ra and Rb can be independently straight or branched alkyl or tertiary alkyl or alkenyl, or aryl hydrocarbon groups such as phenyl, alkyl- or alkenyl- substituted phenyl, or phenyl- substituted alkyl or alkenyl groups. Preferred alkyl and alkenyl groups have short chains eg 5 or less carbon atoms, especially methyl, ethyl, n- or isopropyl, n-, iso- or tert- butyl, and allyl.

Preferred RaRb combinations in RaMRb are those which result in highly volatile compounds which can easily be decomposed in MOVPE systems. Preferred combinations are Ra and Rb both alkyl, eg Ra being methyl and Rb being butyl, or one of Ra or Rb being alkyl and the other being alkenyl, eg Ra being methyl and Rb being allyl. The method of the invention appears to be suitable for the preparation of all RaRb combinations.

It appears that the unsymmetrical dialkyls produced by the method of this invention may combine low temperature decomposition with volatility to allow tellurium containing semiconductors to be grown at relatively low temperatures with higher growth rates. Diallyltelluride has an estimated vapour pressure of only 2 Torr at 450°C and although it decomposes at a lower temperature than allylmethyltelluride the growth rate of CdTe between 240°C-260°C has been reported as 0.6 - 2.0 µ/hr. Dimethyltelluride has a higher vapour pressure, 52 Torr at 25°C but temperatures of ca 500°C are required for growth of CdTe. By comparison, allylmethyltelluride combines a high vapour pressure of 25 Torr at 45°C with a good growth rate, 30 µ/hr at 290°C

Examples illustrating this invention will now be described.

Example 1Preparation of methyltert-butyltellurium from dimethylditelluride and di-tert-butyltellurium

5 Dimethylditelluride (38.1 g) and di-tert-butyltellurium (29.9 g) were mixed in a flask and stirred under nitrogen at ambient temperature for one week. During this time the flask was kept in the dark. The volatile products of the reaction were removed by distillation under reduced pressure giving an orange oil. Distillation of this oil under an atmospheric of nitrogen gave 10 methyltert-butyltellurium as a yellow liquid which boils at 119-122°C. Overall yield = 59%. The identity of the product was confirmed by ^1H and ^{125}Te NMR Spectroscopy. Traces of $\text{t-Bu}_2\text{Te}$ were removed by fractional distillation.

15

Example 2Preparation of allylmethyltellurium from dimethylditelluride and diallyltellurium.

20 Diallyltellurium (15.98 g, 0.076 mol) and dimethylditelluride (25.04 g, 0.088 mol) were mixed in a flask under vacuum and left in the dark for 16 hours at room temperature. The volatile products were removed by warming the reaction mixture to 50°C and distilling at reduced pressure to give 25.63 g of an orange liquid. A second distillation at reduced pressure removed any excess dimethylditelluride giving 22.15 g (0.121 mol) of allylmethyltellurium as a 25 yellow-orange liquid, an overall yield of 79.4 %. The identity of the product was confirmed by ^1H and ^{125}Te NMR spectroscopy.

30

Example 3Preparation of methylisopropyltellurium from dimethyltelluride and di-isopropyltellurium.

35 Dimethyltelluride (5.1 g, 0.018 mol) and di-isopropyltellurium (3.8 g, 0.018 mol) were mixed and kept at room temperature for several days. Removal of the volatile fraction at reduced pressure with

heating gave 4.9 g of a yellow oil. Analysis of this sample by ¹²⁵Te and ¹H nmr spectroscopy showed it to be MeTei-Pr contaminated with ca. 20% of i-Pr₂Te.

5

Example 4

Following the procedure of examples 1, 2 and 3 above isopropylisobutyl tellurium, methylethyltellurium, methylisopropyltellurium, and isopropylisobutyltellurium were also prepared.

10

15

20

CLAIMS

1. A method for the preparation of a tellurium or selenium compound of formula $RaMRb$ wherein M is tellurium or selenium and Ra and Rb are different C_1-C_{20} alkyl, alkenyl or aryl groups, wherein a compound $(Ra)_2M_2$ is reacted with a compound of formula $(Rb)_2M$, in each compound M being the same, followed by isolation of the product $RaMRb$.
2. A method according to claim 1 wherein both Ra and Rb are alkyl groups.
3. A method according to claim 1 wherein one of Ra and Rb is alkyl and the other is alkenyl.
4. A method according to claim 1, 2 or 3 wherein Ra has a lower molecular weight than Rb.
5. A method according to claim 2, 3 or 4 wherein Ra and Rb contain 5 or less carbon atoms.
6. A method according to claim 5 wherein Ra is methyl and Rb is tert-butyl.
7. A method according to claim 5 wherein Ra is methyl and Rb is allyl.
8. A method according to claim 5 wherein Ra is methyl and Rb is iso propyl.
9. A method according to claim 5 wherein Ra is isopropyl and Rb is isobutyl.
10. A method according to any one of claims 1 to 9 wherein the method is carried out in two steps, being a first lower temperature step followed by a second higher temperature step.
11. A method according to any one of claims 1 to 10 wherein M is tellurium.
12. A method for the preparation of a tellurium or selenium compound of formula $RaMRb$ wherein M is tellurium or selenium and Ra and Rb are different C_1-C_{20} alkyl, alkenyl or aryl groups, wherein a compound $(Ra)_2M_2$ is reacted with a compound $(Rb)_2M$, in each compound M being the same, followed by isolation of the product $RaMRb$.
13. A method according to claim 12 wherein both Ra and Rb are alkyl groups.

groups.

14. A method according to claim 13 wherein Ra is methyl and Rb is butyl.
15. A method according to claim 13 wherein one of Ra and Rb is alkyl and the other is alkenyl.
16. A method according to claim 15 wherein Ra is methyl and Rb is allyl.
17. A method according to any one of claims 12 to 16 wherein M is tellurium.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 90/00894

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) ⁶		
According to International Patent Classification (IPC) or to both National Classification and IPC Int.Cl. 5 C07C395/00 ; C07C391/00		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
Int.Cl. 5	C07C	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹		
Category ^o	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
A	EP,A,0285834 (AMERICAN CYANAMID CO.) 12 October 1988 see example 1 <div style="text-align: center; margin-top: 20px;">---</div>	
<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>^o Special categories of cited documents : ¹⁰</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"A" document member of the same patent family</p> </div> </div>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
04 SEPTEMBER 1990	26. 09. 90	
International Searching Authority	Signature of Authorized Officer	
EUROPEAN PATENT OFFICE	Natalie Weinberg	

**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO.**

PCT/GB 90/00894

SA 37484

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

18/09/90

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A-0285834	12-10-88	JP-A- 63283032	18-11-88

EPO FORM P0479

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82